

**ANOMALOUS SULFUR ISOTOPE COMPOSITION OF LUNAR ORANGE GLASS 74002.** J. W. Dottin III<sup>1</sup>, J. Farquhar<sup>2,3</sup>, S.T. Kim<sup>4</sup>, B. Wing<sup>5</sup>, C. Shearer<sup>6</sup> <sup>1</sup>Earth and Planets Laboratory, Carnegie Institution for Science; Washington, DC 20015, USA., <sup>2</sup>Department of Geology, University of Maryland; College Park, MD 20742, USA., <sup>3</sup>Earth System Science Interdisciplinary Center; College Park, MD 20742, USA., <sup>4</sup>School of Earth, Environment & Society, McMaster University; Hamilton, Ontario, Canada., <sup>5</sup>Department of Geological Sciences, University of Colorado Boulder; Boulder, CO 80302, USA., <sup>6</sup>Institute of Meteoritics, University of New Mexico; Albuquerque, NM 87131, USA.

**Introduction:** The earliest atmospheres on Earth and Mars received contributions of volatiles from volcanic outgassing, were optically thin, and were dominated by ultra-violet (UV) photochemistry of gaseous sulfur bearing molecules that results in mass independent fractionation of sulfur (MIF-S) [1, 2]. UV photochemistry was a critical component in the cycling of sulfur on these planets. On Earth, MIF was especially important in establishing sulfur budgets available for the preservation of life.

Lunar volcanism peaked at ~3.8 Ga, consisting of both effusive and pyroclastic style eruptions, which produced both local and global transient lunar atmospheres [3]. The production of these atmospheres can be seen as analogous to the atmosphere's produced on early Earth and Mars. On the Moon, sulfur was consistently contributed to the tenuous atmosphere through magma ocean outgassing and volcanic eruptions [3]. Whether the Moon shares a similar history of sulfur cycling through UV photochemistry in its early evolution, remains unknown. Determining a role for UV chemistry in early lunar atmospheres can shed light on the processes responsible for the distribution of volatiles throughout lunar reservoirs and the establishment of their respective volatile budgets.

To date, high-precision quadruple S-isotope measurements on materials from this period only exist on lunar basalts and show no clear evidence of MIF-S. The isotopic composition of lunar basalts is inferred as homogenous with an average isotopic composition of  $\delta^{34}\text{S} = 0.62 \pm 0.20$ ,  $\Delta^{33}\text{S} = 0.002 \pm 0.010$ ,  $\Delta^{36}\text{S} = 0.030 \pm 0.13$  [4, 5]. Homogeneity of sulfur in lunar basalts implies a well-mixed lunar (upper) mantle. Other materials erupted during the same period, such as lunar glass beads, have not yet been analyzed for quadruple S isotopes. Lunar volcanic glasses are thought to be products of pyroclastic eruptions on the Moon [6]. The glass beads contain a surface coating rich in volatiles associated with condensed gas from the volcanic cloud [7]. Sulfur is a major component of these coatings [7] and the sulfur retains geochemical information associated with how it was processed while in the volcanic plume and can potentially provide direct evidence that UV photochemistry occurred in the volcanic cloud prior to vapor condensation on the glass beads. Sulfur also exists within the glass beads (dissolved into the glass and within melt inclusions) [8, 9]. This S is likely to retain information related to the composition of the melt, providing insight into potential S heterogeneity among multiple mantle sources and S behavior during eruption.

Here, we present S isotope data on sieved fractions of lunar volcanic glass from drive tube 74002/1. Each sample

was sieved into nine grain size fractions and each fraction was processed using the HF + CrCl<sub>2</sub> acid digestion technique to efficiently digest the glassy materials. Using this technique, we were able to extract sulfur trapped within the interior of the glass beads and sulfur coated on the exterior of the glass beads. This is a method that is different from previous work on samples from the same drive tube [10] which used an HCl digestion technique that likely only extracted S from the grain exteriors. With our sulfur isotope measurements, we aim to (1) determine whether there are compositional differences between sulfur captured within the glass and condensed on the glass exterior and (2) provide information on how the S has been processed throughout the history of the glass beads.

**Methods:** Glass beads from drive tube 74002/1 (74002, 2221 and 74001, 2206) were picked for impurities and sieved into 9 grain size fractions. Sample 74001, 2206 was sieved as two stacks (Stack A and B). The reduced sulfur components of 74002, 2221 and 74001, 2206-Stack B were extracted as Ag<sub>2</sub>S using an HF + CrCl<sub>2</sub> digestion method described in [11]. Stack A underwent a sequential extraction of Acid Volatile Sulfur, Chromium Reducible Sulfur, and Thode extraction of S (all as Ag<sub>2</sub>S), to potentially identify and analyze multiple pools of S. For samples that yielded measurable amounts of S during the AVS step, we subjected the residues to the HF + CrCl<sub>2</sub> technique and extracted additional S in this step.

The sulfur extracted as Ag<sub>2</sub>S was subsequently rinsed, dried, and reacted with excess fluorine to produce SF<sub>6</sub>. The product SF<sub>6</sub> was then purified using cryogenic techniques and passed through a gas chromatograph. The purified SF<sub>6</sub> was lastly analyzed on a ThermoFinnigan MAT 253 gas source isotope ratio mass spectrometer.

Isotopic data are reported in ‰ using the following notation and normalized relative to Canyon Diablo Troilite:

$$\delta^{34}\text{S} = [((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{reference}}) - 1]$$

$$\Delta^{33}\text{S} = [(((^{33}\text{S}/^{32}\text{S})_{\text{sample}} / (^{33}\text{S}/^{32}\text{S})_{\text{reference}}) - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{reference}})^{0.515})]$$

$$\Delta^{36}\text{S} = [(((^{36}\text{S}/^{32}\text{S})_{\text{sample}} / (^{36}\text{S}/^{32}\text{S})_{\text{reference}}) - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{reference}})^{1.9})]$$

Uncertainty on  $\delta^{34}\text{S}$  and  $\Delta^{36}\text{S}$  ( $\pm 0.3\text{‰}$ ) is estimated from long-term reproducibility on repeat measurements of international standard IAEA-S1. Uncertainty on  $\Delta^{33}\text{S}$  is estimated from mass spectrometric counts on  $^{33}\text{S}$  ( $\pm 0.016\text{‰}$  and  $\pm 0.008\text{‰}$ , for short and long counting sessions respectively).

**Results:** In 74002, 2221, S concentrations range from 294 ppm to 596 ppm.  $\delta^{34}\text{S}$  compositions range +0.66 to -

1.15,  $\Delta^{33}\text{S}$  ranges from -0.014 to -0.036, and  $\Delta^{36}\text{S}$  ranges from 0.52 to 2.17. AVS from 74001, 2206 Stack A exhibit S concentrations ranging from 183 to 26 ppm,  $\delta^{34}\text{S} = -3.11$  and -2.64 for the >20  $\mu\text{m}$  and >45  $\mu\text{m}$  fraction respectively,  $\Delta^{33}\text{S} = -0.030$  and -0.025 for the >20  $\mu\text{m}$  and >45  $\mu\text{m}$  fraction respectively, and  $\Delta^{36}\text{S} = -0.16$  and -0.01 for the >20  $\mu\text{m}$  and >45  $\mu\text{m}$  fraction, respectively. Stack A residues yielded S concentrations ranging from 131 to 109 ppm,  $\delta^{34}\text{S} = -0.60$  and -1.34,  $\Delta^{33}\text{S} = -0.015$  and -0.011, and  $\Delta^{36}\text{S} = 0.66$  and 0.37 for the >20  $\mu\text{m}$  and >45  $\mu\text{m}$  fraction respectively. Sulfur from 74001, 2206 stack B was extracted from sieve fractions ranging from >10  $\mu\text{m}$  to >150  $\mu\text{m}$  and S concentrations ranged from 244 to 100 ppm. We were able to reliably analyze S from fractions ranging from >10  $\mu\text{m}$  to >75  $\mu\text{m}$  and observe  $\delta^{34}\text{S} = -2.11$  to -1.71,  $\Delta^{33}\text{S} = 0.003$  to -0.019, and  $\Delta^{36}\text{S} = 0.52$  to 2.17.

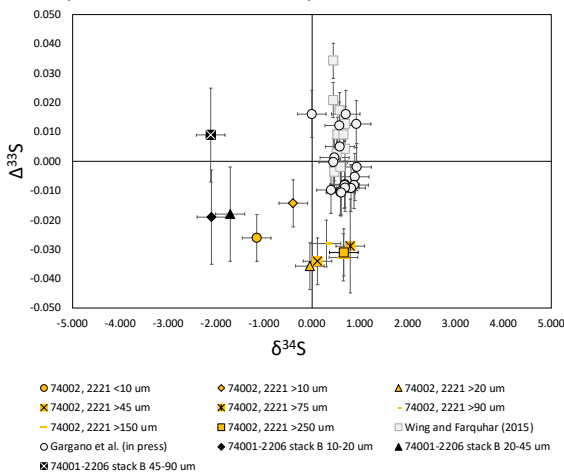


Figure 1. S isotope compositions of lunar glasses and basalts.

**Discussion:** The variability in  $\delta^{34}\text{S}$  values for 74002 and 74001 can be readily linked to isotopic fractionation during degassing, in agreement with previous assertions by (10). In plots of  $\delta^{34}\text{S}$  vs. Fraction Remaining (of estimated initial S content of 600 ppm), most data for 74002 can be fit using a degassing model with an  $\alpha_{\text{gas-melt}} = 1.0016$ . Data that are not fit with the curve are associated with the smallest grain size fractions and likely due to a more pronounced contribution of sulfur from condensed vapor rather than the interior. Furthermore, our suggestion is readily observed in our sequential extraction of 74001, 2206 where the composition associated with the interior of the grain is fit with the curve and the composition associated with the exterior of the grain falls off the curve.

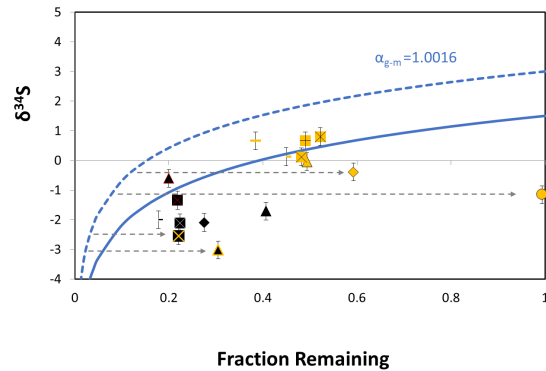


Figure 2. Sulfur degassing model for 74002, 2221 and 74001, 2206. Dashed line= gas composition. Solid line= melt composition.

The  $\Delta^{33}\text{S}$  compositions among orange and black glasses are homogenous, yet distinct from one another. The black glasses preserve strictly mass dependent  $\Delta^{33}\text{S}$  ( $\Delta^{33}\text{S} = -0.008 \pm 0.006$  2SE), whereas the orange glass beads preserve a mass-independent composition ( $\Delta^{33}\text{S} = -0.029 \pm 0.004$  2SE), that is different from the composition measured among mare basalts ( $\Delta^{33}\text{S} = 0.002 \pm 0.004$  2SE). There are two possibilities for this anomalous observation. The first possibility is that the  $\Delta^{33}\text{S}$  may have been captured upon condensation of a photolytic component in the volcanic cloud. The second possibility is that we are observing mantle heterogeneity. The anomalous signature associated with 74002, 2221 is not consistent with addition of any anomalous sulfur component because there is no evidence of mixing between the anomalous sulfur compositions and the assumed composition of the lunar mantle ( $\Delta^{33}\text{S} = 0.002 \pm 0.004$  2SE, lunar basalts [4,5]). Instead, we argue that the composition measured in 74002, 2221 is best associated with an exogenous lunar mantle source. Our hypothesis requires (a) the sulfur erupted from this melt source to have been photochemically processed early in lunar evolution [12] and delivered to the lunar mantle through an unknown mechanism or (b) a process that establishes an inherently different primordial mantle composition between the Earth and Moon. Although the orange and black glasses have been long considered to be related and predominantly reflect differences in devitrification (6), the discrepancy in  $\Delta^{33}\text{S}$  composition among the two samples calls into question their relationship or whether the melt source is isotopically heterogeneous.

**References:** [1] J. Farquhar et al. (2000) *Nature*. 404, 50–52. [2] H.B. Franz et al. 2014 *Nature*, 508, 364–8. [3] D. H. Needham and D. A. Kring (2017) *EPSL* 478, 175–178. [4] A. Gargano et al. (2022) *Am. Min. in press*. [5] B. Wing and J. Farquhar (2015) *GCA* 170, 266–280. [6] G.H. Heiken et al. (1974) *GCA* 38, 1703–1718. [7] C.M. Weitz et al. (1999) *MAPS* 34, 527–540. [8] A. E. Saal and E. H. Hauri (2021) *Sci. Adv.* 7, eabe4641. [9] Saal et al. (2008) *Nature* 454, 192–195. [10] Ding et al. (1983) *GCA* 47, 491–496. [11] Dottin et al. (2021) *Gcubed* 22(6), p.e2021GC009816. Saxena et al. (2017) *EPSL* 474, 198–205.